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(54) ***Process for stabilization of hydrogen silsesquioxane resin solutions***

Verfahren zur Stabilisierung von Wasserstoff-Silsesquioxaneharz- Lösungen

Procéde pour stabilization des solutions de résine de hydrogène silsesquioxane

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(56) References cited:
EP-A- 0 443 760 **EP-A- 0 516 144**

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EP 0 616 001 B1

Description

The present invention relates to solutions of hydrogen silsesquioxane resin which are stable on extended storage. These stable solutions are obtained by incorporating small amounts of acids in the solution.

Hydrogen silsesquioxane resin (H-resin) is known in the art to be a useful precursor to silica-containing ceramic coatings. For instance, U.S. Patent No. 4,756,977 describes a process for forming such a coating in which H-resin is diluted in a solvent, applied to a substrate and ceramified by heating.

Various methods for producing H-resin are also known in the art. For example, U.S. Patent No. 3,615,272 describes a process which comprises adding trichlorosilane to a reaction medium comprising sulfuric acid and an aromatic hydrocarbon, washing the reaction mixture until neutral and recovering the condensed H-resin. Despite the fact that the reference teaches hydrolysis and condensation in an acid, the resultant product is neutralized to prevent gelation.

U.S. Patent No. 5,010,159 teaches a similar process in which a hydridosilane is reacted in an arylsulfonic acid hydrolysis medium followed by separating the resultant H-resin and then contacting it with a neutralizing agent.

The shelf life of the above solvent-diluted H-resins can be unreliable if the resin undergoes crosslinking and increases in molecular weight. We have now found that the incorporation of an acid in the H-resin solution limits the possibility of changes in the molecular weight of the resin.

The present invention provides a method of stabilising a hydrogen silsesquioxane resin solution comprising 0.1 to 100 parts by weight hydrogen silsesquioxane resin in 100 parts by weight solvent characterised in that 0.002 to 4 parts by weight acid are added to said resin solution.

At the time of our invention, the predominant thought within the prior art was that solutions of H-resin must be completely neutralized to prevent any degree of gelation during storage. This belief was a substantial prejudice against the applicant's present claims which are based upon our unexpected finding that such solutions can, in fact, be stabilized for storage by the addition of small amounts of acids.

As used in this disclosure, the expressions "stable" or "stabilized" H-resin solutions are used to describe those solutions in which the molecular weight of the H-resin changes less over time than those which have not been stabilized. It is preferred that the "stable" solutions not gel. It is more preferred that the weight average molecular weight (Mw) of the "stable" solutions not change more than 100%. It is most preferred that the Mw of the "stable" solutions not change more than 25%.

The H-resins which may be used in this invention include hydridosiloxane resins of the formula $HSi(OH)_x(OR)_yO_{z/2}$, in which each R is independently an organic group or a substituted organic group which, when bonded to silicon through the oxygen atom, forms a hydrolyzable substituent, $\underline{x}$ 0-2, $\underline{y}$ = 0-2, $\underline{z}$ = 1-3, $\underline{x} + \underline{y} + \underline{z} = 3$. Examples of R include alkyls such as methyl, ethyl, propyl and butyl; aryls such as phenyl and alkenyls such as allyl or vinyl. As such, these resins may be fully condensed $(HSiO_{3/2})_n$ or they may be only partially hydrolyzed (i.e., containing some Si-OR) and/or partially condensed (i.e., containing some Si-OH). Although not represented by this structure, these resins may also contain a small number (eg., less than about 10%) of silicon atoms which have either 0 or 2 hydrogen atoms attached thereto due to various factors involved in their formation or handling.

The above H-resins and methods for their production are known from the aforementioned patents. For example, U.S. Patent No. 3,615,272 teaches the production of a nearly fully condensed H-resin (which may contain up to 100-300 ppm silanol) by a process comprising hydrolyzing trichlorosilane in a benzenesulfonic acid hydrate hydrolysis medium and then washing the resultant resin with water and/or aqueous sulfuric acid. Similarly, U.S. Patent No. 5,010,159, describes an alternative method comprising hydrolyzing hydridosilanes in an arylsulfonic acid hydrate hydrolysis medium to form a resin which is separated, washed and contacted with a neutralizing agent.

Other hydridosiloxane resins, such as those described in U.S. Patent No. 4,999,397 are produced by hydrolyzing an alkoxy or acyloxy silane in an acidic, alcoholic hydrolysis medium. Any other equivalent hydridosiloxane will also function herein, such as those covered by JP-A [Kokai] Nos. 59-178749, 60-86017 and 63-107122.

In a preferred embodiment of the invention, specific molecular weight fractions of the above H-resins may also be used in this process. Such fraction and methods for their preparation are taught in U.S. Patent No. 5,063,267. Alternative approaches, however, are also contemplated. For example, fractions can also be obtained by a non-solvent precipitation process wherein the H-resin is dissolved in a non-polar solvent such as toluene followed by adding a polar solvent such as acetonitrile thereto to precipitate a fraction of the resin. Since this precipitation process progressively precipitates lower molecular weight fractions with higher concentrations of the polar solvent, the process often involves first precipitating and removing the undesired higher molecular weight fractions from the solution followed by precipitating and collecting the desired fraction and leaving the undesired low molecular weight fractions in solution. A preferred fraction comprises material wherein at least 75% of the polymeric species have a weight average molecular weight above 1200 and a more preferred fraction comprises material wherein at least 75% of the polymeric species have a weight average molecular weight between 1200 and 50,000 (relative to polydimethylsiloxane standards).

According to the present invention, the H-resin is merely dissolved in a solvent to form a solution. Various facilitating measures such as stirring and/or heating may be used as necessary. Solvents which may be used include any agent

or mixture of agents which will dissolve the H-resin to form a homogenous liquid mixture. These solvents include alcohols such as ethyl or isopropyl, aromatic hydrocarbons such as benzene or toluene, alkanes such as n-heptane or dodecane, ketones such as methylisobutylketone, esters, glycol ethers or cyclic dimethylpolysiloxanes. Particularly preferred herein is methylisobutylketone.

The above solvents are used in an amount sufficient to dissolve the H-resin to the concentration desired for application. Generally, enough of the above solvent is used to form a 0.1-50 wt. percent solids solution (i.e., 100 parts by weight solvent and 0.1 to 100 parts by weight H-resin).

As noted above, H-resin solutions of the prior art may be unstable and undergo molecular weight shifts which may not be desirable (e.g., the material may deposit a thicker coating or the material may partially or completely gel). This instability is dependant on factors such as water, impurities, atmospheric humidity, fractionation and temperature. For example, fractionated material is stable for 3-4 months under refrigeration (e.g., 0°C.) whereas it is only stable for 1.5 months at room temperature.

According to the present invention, it has been discovered that the addition of a small amount of acid to these solutions can dramatically affect their stability and shelf-life. Although not wishing to be bound by theory, applicants postulate that both the acidity and the chemical reactions (e.g., oxidation, chemical complexing and the like) of the acids contribute to the stabilizing of H-resin solutions.

The acids which can be used herein are any which have the desired stabilizing effect without adversely affecting the resin. These include inorganic acids such as boric, carbonic, hydrochloric, iodic, nitric, nitrous, phosphoric, phosphorous, sulfuric and sulfurous as well as organic acids such as acetic, benzoic, butyric, citric, formic, lactic, maleic, naphthoic, oxalic, phthalic, picric, propionic, succinic, tartaric, toluic, toluene sulfonic and trifluoroacetic. Of these, nitric acid is particularly preferred.

The above acids are added to the solution in an amount effective to stabilize the H-resin. This amount can vary over a wide range depending on the acid and the above factors. Generally, however, the acids are added in an amount of between 0.002 and 4 parts per weight and, preferably, between 0.01 and 0.1 parts per weight, based on the total weight of solution.

It should be noted that the order of mixing the acid, solvent and H-resin is not critical. For example, in addition to the order described above, the H-resin may be simply dissolved in a solvent-acid mixture.

In addition, the solutions of the present invention may also contain other ingredients such as ceramic oxide precursors. Examples of such precursors include compounds of various metals such as aluminum, titanium, zirconium, tantalum, niobium and/or vanadium as well as various non-metallic compounds such as those of boron or phosphorous. These precurors may be dissolved in solution, hydrolyzed and subsequently pyrolyzed, at relatively low temperatures and relatively rapid reaction rates to form ceramic oxide coatings.

The above ceramic oxide precursor compounds generally have one or more hydrolyzable groups bonded to the above metal or non-metal, depending on the valence of the metal. The number of hydrolyzable groups to be included in these compounds is not critical as long as the compound is soluble in the solvent. Likewise, selection of the exact hydrolyzable substituent is not critical since the substituents are either hydrolyzed or pyrolyzed out of the system. Typical hydrolyzable groups include alkoxy such as methoxy, propoxy, butoxy and hexoxy; acyloxy such as acetoxy or other organic groups bonded to said metal or non-metal through an oxygen such as acetylacetonate. Specific compounds, therefore, include zirconium tetracetylacetonate, titanium dibutoxy diacetylacetonate, aluminum triacetylacetonate and tetraisobutoxy titanium.

When the H-resin solution is to be combined with one of the above ceramic oxide precursors, generally it is used in an amount such that the final ceramic coating contains 0.1 to 30 percent by weight of the modifying ceramic oxide.

The solution may also contain a platinum, rhodium or copper catalyst to increase the rate and extent of conversion to silica. Generally, any platinum, rhodium or copper compound or complex which can be solubilized will be functional. For instance, a composition such as platinum acetylacetonate, rhodium catalyst $RhCl_3[S(CH_2CH_2CH_2CH_3)_2]_3$, obtained from Dow Corning Corporation, Midland, Michigan, or cupric naphthenate are suitable within this invention. These catalysts are generally added in an amount of between 5 to 1000 ppm, preferably 5 to 500 ppm, platinum, rhodium or copper based on the weight of H-resin.

The resultant stabilized solutions are useful for forming coatings on various substrates, especially electronic devices.

The following non-limiting example is provided so that those skilled in the art will more readily understand the invention.

Example

Hydrogen silsesquioxane resin was made by the process described in US Patent No. 3,615,272. Generally, the process comprised slowly adding trichlorosilane to an agitated toluene sulfonic acid hydrate hydrolysis medium. After hydrolysis was complete, the hydrolysis medium was settled and the organic layer (containing the H-resin) was sep-

arated and removed. The organic layer was washed twice with sulfuric acid and twice with water and then filtered and stripped to about 20 wt% solids in toluene.

The H-resin solution was then fractionated by adding acetonitrile to the solution to precipitate out the undesired high molecular weight fractions. The desired molecular weight fraction was then precipitated out of the solution by adding additional acetonitrile.

Two samples were prepared in the above manner and their properties are listed in Table 1 at time 0 (Samples A and B).

The resultant resins were then treated with the acids and their concentrations listed in Table 1 (with a control). Gel Permeation Chromatography (GPC) was run on the resins (relative to a polydimethylsiloxane standard) at the times listed in the Table (elapsed time) and the results recorded.

As is evident from the data, the addition of an acid to the resin solution clearly inhibits the former molecular weight shifts of the art which were indicative of instability.

TABLE 1: Acid Stabilization of Hydrogensilsesquioxane Solutions in Methyl Isobutyl Ketone @ 25 C

RESIN LOT#	ACID TYPE	ACID CONC (ppm)	PERCENT SOLIDS (%)	ELAPSED TIME (days)	Mn	Mw	Mw/Mn	Low Mw	High Mw
A	NONE	0	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	13	7376.7	23189.0	3.144	299	323443
			20.00	32	6671.4	44880.2	6.724	175	705585
			20.00	46	8960.6	72313.6	8.070	222	1235785
			20.00	60	9030.1	97680.2	10.815	258	1504915
			20.00	73	9033.1	107622.6	11.914	258	1450911
			20.00	95	8751.3	155841.7	17.808	256	1994484
			20.00	110			NOT FILTERABLE		
			20.00	123	9658.0	187569.9	19.419	325	2268874
			20.00	131	8969.7	181505.6	20.236	316	1885182
			20.00	144	5964.2	170787.0	28.638	188	1994484
A	HNO3	211	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	13	6613.6	13086.1	1.979	307	86438
			20.00	32	5645.8	12784.3	2.264	179	94193
			20.00	46	6045.6	11433.0	1.891	201	92251
			20.00	60	6020.7	12930.6	2.148	258	99061
			20.00	73	6338.6	13113.6	2.069	258	92251
			20.00	95	5913.0	14056.6	2.377	256	108793
			20.00	110	5523.0	14689.7	2.660	252	143114
			20.00	123	6522.0	15736.6	2.413	225	138192
			20.00	131	5473.7	15617.3	2.853	316	133275
			20.00	144	4672.6	16518.6	3.535	198	157917
A	HNO3	921	SOLID	0	6418.8	12226.9	1.906	307	74845
			20.00	13	6672.3	13095.3	1.963	312	94193
			20.00	32	5661.0	12574.1	2.221	179	94193
			20.00	46	6159.0	12028.0	1.953	205	94193
			20.00	60	5828.0	12318.2	2.114	258	86438
			20.00	73	5511.4	12163.0	2.207	258	94241
			20.00	95	5885.2	12482.7	2.121	258	85468
			20.00	110	4872.6	12327.4	2.530	252	94183
			20.00	123	5540.9	12610.6	2.276	225	103918
			20.00	131	5021.9	12245.2	2.438	318	84501
			20.00	144	4000.7	12318.2	3.079	198	94193
A	BENZOIC	231	SOLID	0	6418.6	12226.9	1.906	307	74846
			20.00	13	7323.5	23942.1	3.269	307	303185
			20.00	32	6344.0	44083.3	6.949	175	632454
			20.00	46	8705.2	63584.3	7.302	209	1126804
			20.00	60	9141.9	81204.2	8.883	258	1450911
			20.00	73	7387.3	89158.1	12.069	258	1398992
			20.00	95	8638.2	129935.8	15.042	258	1687428
			20.00	110	8710.6	153372.2	17.608	248	1830634
			20.00	123	10122.2	175250.2	17.313	325	2434234
			20.00	131	8808.4	163357.7	18.546	320	1885182
			20.00	144	6410.5	185282.5	28.903	198	2104051
A	BENZOIC	952	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	13	7484.9	30814.3	4.117	295	394788
			20.00	32	7494.0	109574.0	14.622	175	1687428
			20.00	46	10367.7	170529.0	16.448	188	2104051
			20.00	60	9713.4	211498.9	21.774	252	2434234
			20.00	73			NOT FILTERABLE		
			20.00	83			SOLUTION GELLED		
A	H3PO4	187	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	7			SOLUTION GELLED		
A	H3PO4	1110	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	4			SOLUTION GELLED		
A	F3CCOOH	192	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	13	6981.0	14066.0	2.015	312	123462
			20.00	32	6270.4	16629.2	2.652	198	152977
			20.00	46	7191.9	20026.5	2.785	222	192645
			20.00	60	6339.5	15387.5	2.427	260	143114
			20.00	73	6795.5	32924.7	4.845	258	394563
			20.00	95	7606.6	56495.3	7.427	258	918157
			20.00	110	8063.8	81030.3	10.049	248	1236785
			20.00	123	9214.4	103236.6	11.204	329	1450911
			20.00	131	9713.4	121992.2	12.559	318	1559006
			20.00	144	7185.6	147451.0	20.520	198	1885182
A	F3CCOOH	952	SOLID	0	6418.8	12226.9	1.905	307	74846
			20.00	13	6413.2	13342.4	2.080	312	123462
			20.00	32	5353.6	13368.8	2.497	184	123462
			20.00	46	6287.3	13809.4	2.193	195	118565
			20.00	60	7423.6	27213.2	3.666	260	313298
			20.00	73	6827.9	16584.6	2.428	258	143114
			20.00	95	7687.2	21304.8	2.779	258	190654
			20.00	110	6259.6	25208.1	4.027	252	272844
			20.00	123	7524.6	30964.2	4.115	316	405023
			20.00	131	6833.4	34145.9	4.997	316	405023
			20.00	144	5846.6	43498.1	7.440	198	632454

TABLE 1 (cont.): Acid Stabilization of Hydrogensilsesquioxane Solutions in Methyl Isobutyl Ketone @ 25 C

RESIN LOT #	ACID TYPE	ACID CONC (ppm)	PERCENT SOLIDS (%)	ELAPSED TIME (days)	Mn	Mw	Mw/Mn	Low Mw	High Mw
A	H3BO3	289	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	6599.4	13342.4	2.022	299	99051
			20.00	32	5739.0	13882.7	2.419	179	103918
			20.00	46	6442.9	14341.0	2.228	188	143114
			20.00	60	6817.1	15360.0	2.263	260	148043
			20.00	73	6218.2	15911.5	2.559	256	148043
			20.00	95	6124.8	18039.6	2.945	256	172770
			20.00	110	6626.4	19573.2	2.954	252	192645
			20.00	123	6953.1	21341.9	3.069	325	222598
			20.00	131	6558.9	22288.1	3.398	316	212598
			20.00	144	5124.7	23728.2	4.630	179	217595
A	H3BO3	914	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	6752.3	13150.2	1.947	307	94193
			20.00	32	6125.7	13177.6	2.151	201	94678
			20.00	46	4752.9	11797.9	2.482	188	99051
			20.00	60	6362.9	13848.1	2.176	256	133275
			20.00	73	6217.3	14194.3	2.283	256	133275
			20.00	95	5523.9	15148.7	2.742	256	143114
			20.00	110	5567.5	16187.4	2.897	252	164843
			20.00	123	6255.7	17183.5	2.700	325	167814
			20.00	131	6163.5	18233.4	2.958	316	157917
			20.00	144	4733.3	19471.4	4.114	198	172770
A	p-TSA	183	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	6682.1	12866.6	1.926	307	92251
			20.00	32	5594.7	12336.5	2.205	184	85488
			20.00	46	5528.4	11387.5	2.060	188	93222
			20.00	60	5337.6	12035.2	2.255	256	94678
			20.00	73	4844.9	11907.4	2.458	256	94241
			20.00	95	4560.2	11843.5	2.597	256	93222
			20.00	110	4461.2	11807.0	2.647	252	94193
			20.00	123	4761.9	11807.0	2.479	325	89342
			20.00	131	3880.6	12190.4	3.141	188	94193
			20.00	144	3826.4	12448.1	3.253	198	94678
A	p-TSA	990	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	6428.5	12758.9	1.984	307	94193
			20.00	32	4493.3	12035.2	2.678	201	94193
			20.00	46	4521.8	11423.9	2.526	201	84501
			20.00	60	4992.4	12638.0	2.531	256	94678
			20.00	73	4636.0	13067.8	2.819	256	133275
			20.00	95	4489.7	14680.5	3.270	256	138192
			20.00	110	4275.8	15102.8	3.532	248	157917
			20.00	123	4581.9	16242.7	3.560	320	172770
			20.00	131	4388.9	19785.9	4.508	188	192645
			20.00	144	4009.6	21518.0	5.367	198	282937
A	ACETIC	192	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	7468.7	24779.7	3.318	312	293044
			20.00	32	6617.4	52261.6	7.898	192	863313
			20.00	46	9033.1	77890.2	8.601	222	1289426
			20.00	60	9314.1	103139.2	11.073	256	1559008
			20.00	73	9804.2	130034.0	13.263	256	1559008
			20.00	110	9087.5	180114.8	19.820	248	2104051
			20.00	123	10440.4	194836.5	18.662	329	2213872
			20.00	131	8869.1	174456.5	19.670	320	1939799
			20.00	144	6448.3	183393.7	28.441	184	1776158
A	ACETIC	1019	SOLID	0	6416.8	12228.9	1.905	307	74848
			20.00	13	7758.4	31685.1	4.084	299	394788
			20.00	32	7387.5	104015.9	14.080	171	1450911
			20.00	46	9788.1	172076.0	17.584	184	1939799
			20.00	60	9740.7	211097.3	21.672	260	2379056
			20.00	73	7280.2	180710.8	24.822	256	1994484
			20.00	94	SOLUTION GELLED				

TABLE 1 (cont.): Acid Stabilization of Hydrogensilsesquioxane Solutions in Methyl Isobutyl Ketone @ 25 C

RESIN LOT #	ACID TYPE	ACID CONC (ppm)	PERCENT SOLIDS (%)	ELAPSED TIME (days)	Mn	Mw	Mw/Mn	Low Mw	High Mw
B	NONE	0	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4094.1	11269.0	2.752	282	75810
			20.00	28	4348.8	11715.8	2.694	269	80634
			20.00	42	4178.7	12007.8	2.874	265	84501
			20.00	56	3892.2	12238.0	3.144	256	99051
			20.00	69	3881.5	12857.5	3.312	256	94193
			20.00	91	4619.0	14331.9	3.103	256	108793
			20.00	105	4569.1	15332.4	3.356	256	143114
			20.00	119	4955.7	16343.9	3.298	325	157917
			20.00	127	4501.3	16668.1	3.703	256	152977
			20.00	140	4076.3	16933.2	4.154	248	152977
B	HNO3	170	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4216.8	11341.9	2.690	286	71958
			20.00	28	4127.1	11241.8	2.724	256	81117
			20.00	42	4032.1	11223.4	2.783	265	79889
			20.00	56	4006.9	11414.8	2.849	265	81600
			20.00	69	3589.3	11907.4	3.317	256	84501
			20.00	91	4479.0	12628.8	2.820	256	94193
			20.00	105	4477.2	13040.4	2.913	266	94678
			20.00	119	4571.8	13992.7	3.061	329	128366
			20.00	127	4347.1	13937.7	3.206	265	113678
			20.00	140	4120.8	13928.5	3.380	299	128366
B	HNO3	456	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4255.3	11323.7	2.661	299	75810
			20.00	28	4208.3	11223.4	2.667	269	75810
			20.00	42	4188.7	11250.7	2.686	273	77738
			20.00	56	4033.6	10913.7	2.706	265	75810
			20.00	69	3745.6	11305.4	3.018	256	76774
			20.00	91	4315.9	11341.9	2.628	260	75810
			20.00	105	4305.2	11232.5	2.609	258	79889
			20.00	119	4517.3	11524.2	2.551	329	94193
			20.00	127	4039.6	11469.5	2.839	260	81600
			20.00	140	3841.5	11068.7	2.881	273	74846
B	BENZOIC	100	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4096.6	11177.6	2.728	286	76703
			20.00	28	4493.3	11962.1	2.662	265	80634
			20.00	42	4148.4	12117.3	2.921	256	86436
			20.00	56	4226.8	12683.8	3.001	269	99051
			20.00	69	4054.1	13232.5	3.264	256	99051
			20.00	91	4666.3	14781.4	3.168	256	123462
			20.00	105	4663.7	15433.5	3.309	256	143114
			20.00	119	4995.9	16822.8	3.367	325	157917
			20.00	127	4763.6	17615.2	3.698	273	182883
			20.00	140	4661.9	18214.9	3.907	269	182883
B	BENZOIC	490	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4251.7	11378.3	2.676	290	75810
			20.00	28	3964.2	11825.2	2.983	273	89342
			20.00	42	3971.3	11524.2	2.902	265	77738
			20.00	56	4191.2	12766.0	3.046	256	99051
			20.00	69	4432.6	13552.9	3.058	256	94241
			20.00	91	4621.7	14653.0	3.170	258	138192
			20.00	105	4683.3	15516.2	3.313	256	143114
			20.00	119	5122.0	16702.9	3.261	325	140160
			20.00	127	4586.9	17200.4	3.750	269	148043
			20.00	140	4446.9	17827.4	4.009	273	157917
B	H3PO4	170	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	5555.3	16868.7	3.037	290	2104051
			20.00	13	SOLUTION GELLED				
B	H3PO4	560	SOLID	0	4120.8	10804.4	2.622	282	67162
			20.00	9	4283.8	11360.1	2.652	290	74846
			20.00	28	4145.8	11159.8	2.692	273	79889
			20.00	42	4150.2	11341.9	2.733	269	80634
			20.00	56	4001.6	11450.4	2.861	273	92251
			20.00	69	3822.0	11925.8	3.120	258	89342
			20.00	91	4499.5	12409.6	2.758	260	93222
			20.00	105	4408.5	13012.9	2.952	256	94193
			20.00	119	4694.0	13800.2	2.940	329	113678
			20.00	127	4411.2	14148.5	3.207	265	118565
			20.00	140	4339.0	15178.2	3.498	269	143114
B	F3CCOOH	138	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4342.6	11542.5	2.658	290	76774
			20.00	28	4195.6	11734.0	2.797	269	81600
			20.00	42	4158.2	12117.3	2.914	265	89342
			20.00	56	4128.2	12656.3	3.066	260	99051
			20.00	69	4223.2	13580.4	3.216	256	94678
			20.00	91	4951.2	15213.0	3.073	273	143114
			20.00	105	4802.9	16123.0	3.357	256	152977
			20.00	119	5185.5	17569.1	3.388	329	167814
			20.00	127	4710.1	17762.8	3.771	269	148043
			20.00	140	4658.2	18759.7	4.026	273	172770

TABLE 1 (cont.): Acid Stabilization of Hydrogensilsesquioxane Solutions in Methyl Isobutyl Ketone @ 25 C

RESIN LOT #	ACID TYPE	ACID CONC (ppm)	PERCENT SOLIDS (%)	ELAPSED TIME (days)	Mn	Mw	Mw/Mn	Low Mw	High Mw
B	F3CCOOH	486	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4194.7	11378.3	2.713	290	76774
			20.00	28	4082.4	11442.2	2.798	265	75810
			20.00	42	4089.7	11697.5	2.860	265	80634
			20.00	56	3938.4	11962.1	3.037	260	90312
			20.00	69	3918.0	12665.5	3.233	256	93222
			20.00	91	4705.6	14524.5	3.087	256	118565
			20.00	105	4823.5	15773.6	3.270	256	152977
			20.00	119	5131.8	16905.5	3.294	329	152977
			20.00	127	4646.7	17421.6	3.749	290	157917
			20.00	140	4505.7	18298.0	4.061	265	167814
B	H3BO3	110	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4173.4	11088.7	2.657	290	74846
			20.00	28	4023.8	11405.7	2.836	265	77738
			20.00	42	4340.8	11697.5	2.695	265	84501
			20.00	56	4280.2	12053.4	2.816	269	92251
			20.00	69	3823.8	12446.1	3.255	256	92251
			20.00	91	4661.9	13380.7	2.868	260	94193
			20.00	105	4510.2	13763.6	3.052	256	108793
			20.00	119	4988.4	14827.3	2.986	325	133275
			20.00	127	4438.9	14854.9	3.347	299	118565
			20.00	140	4414.8	15755.2	3.569	265	143114
B	H3BO3	445	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	6	SOLUTION GELLED				
B	p-TSA	180	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4252.6	11295.3	2.656	295	74846
			20.00	28	4216.1	10958.2	2.599	273	69553
			20.00	42	3987.4	10804.4	2.710	265	74846
			20.00	56	3750.9	10522.3	2.805	260	70034
			20.00	69	3740.2	11013.9	2.945	256	74846
			20.00	91	4283.8	10877.3	2.539	260	74846
			20.00	105	4309.6	10804.4	2.507	278	80634
			20.00	119	4368.4	10895.5	2.494	325	74846
			20.00	127	3950.9	11032.1	2.792	248	80634
			20.00	140	3691.4	10576.9	2.865	265	72920
B	p-TSA	550	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4182.1	11167.0	2.669	288	74846
			20.00	28	3926.0	10904.6	2.778	269	84501
			20.00	42	3740.2	10631.5	2.842	265	74846
			20.00	56	3437.6	10304.0	2.997	260	72882
			20.00	69	3454.4	11004.8	3.186	256	84501
			20.00	91	4208.1	11241.6	2.671	260	78703
			20.00	105	3968.9	11004.8	2.774	260	77738
			20.00	119	4139.5	11542.5	2.788	329	94193
			20.00	127	3958.0	12391.3	3.131	256	94241
			20.00	140	3705.6	12281.7	3.314	269	92251
B	ACETIC	148	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4286.5	11332.8	2.644	288	74846
			20.00	28	4247.3	11852.6	2.791	265	84501
			20.00	42	4422.8	12327.4	2.787	265	89342
			20.00	56	4112.8	12574.1	3.057	260	99051
			20.00	69	4407.7	13552.9	3.075	256	103918
			20.00	91	4715.4	14726.4	3.123	260	128365
			20.00	105	4788.7	15746.0	3.288	256	133275
			20.00	119	4910.1	16684.5	3.398	325	143114
			20.00	140	4371.1	17587.6	4.024	252	152977
B	ACETIC	577	SOLID	0	4120.8	10804.4	2.622	282	67152
			20.00	9	4213.4	11323.7	2.688	295	74846
			20.00	28	4406.6	12099.1	2.745	282	91281
			20.00	42	4075.4	12144.7	2.980	265	87889
			20.00	56	4160.0	12811.7	3.080	260	94678
			20.00	69	3880.6	13738.1	3.540	256	103918
			20.00	91	4725.3	15295.7	3.237	256	128365
			20.00	105	4626.2	16150.6	3.491	256	143114
			20.00	119	5044.2	17467.7	3.463	325	152977
			20.00	127	4756.5	18261.1	3.839	260	143114
			20.00	140	4337.3	18556.5	4.278	248	187814

Claims

1. A method of stabilising a hydrogen silsesquioxane resin solution comprising 0.1 to 100 parts by weight hydrogen silsesquioxane resin in 100 parts by weight solvent characterised in that 0.002 to 4 parts by weight acid are added to said resin solution.

2. A method according to claim 1 wherein at least 75% of the polymeric species of the resin have a weight average molecular weight above 1200.

3. A method according to claim 2 wherein at least 75% of the polymeric species of the resin have a weight average molecular weight between 1200 and 50,000.

4. A method according any of claims 1 to 3, wherein the solvent is selected from alcohols, aromatic hydrocarbons, alkanes, ketones, esters, glycol ethers and cyclic dimethylpolysiloxanes.

5. A method according to any of claims 1 to 4, wherein the acid is selected from boric, carbonic, hydrochloric, iodic, nitric, nitrous, phosphoric, phosphorous, sulfuric and sulfurous acids.

6. A method according to any of claims 1 to 4, wherein the acid is selected from acetic, benzoic, butyric, citric, formic, lactic, maleic, naphthoic, oxalic, phthalic, picric, propionic, succinic, tartaric, toluic, toluene sulfonic and trifluoro-acetic acids.

7. A method according to any of claims 1 to 6, wherein the acid is added in an amount between 0.01 to 0.1 parts by weight.

8. A method according to any of claims 1 to 7, wherein the resin solution further comprises modifying ceramic oxide precursors comprising a compound containing an element selected from titanium, zirconium, aluminum, tantalum, vanadium, niobium, boron and phosphorous wherein the compound contains at least one hydrolyzable substituent selected from alkoxy or acyloxy and the compound is present in an amount such that the coating contains 0.1 to 30 percent by weight modifying ceramic oxide.

9. A method according to any of claims 1 to 7, wherein the resin solution further comprises a platinum, rhodium or copper catalyst in an amount of between 5 to 1000 ppm platinum, rhodium or copper based on the weight of hydrogen silsesquioxane resin.

Patentansprüche

1. Verfahren zur Stabilisierung einer Hydrogensilsesquioxanharz-Lösung, die 0,1 bis 100 Gewichtsteile Hydrogensilsesquioxanharz in 100 Gewichtsteilen Lösemittel enthält, dadurch gekennzeichnet, daß der Harzlösung 0,002 bis 4 Gewichtsteile Säure zugesetzt werden.

2. Verfahren nach Anspruch 1, wobei mindestens 75 % der polymeren Moleküle des Harzes ein gewichtsdurchschnittliches Molekulargewicht von mehr als 1.200 haben.

3. Verfahren nach Anspruch 2, wobei mindestens 75 % der polymeren Moleküle des Harzes ein gewichtsdurchschnittliches Molekulargewicht zwischen 1.200 und 50.000 haben.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Lösemittel ausgewählt ist aus Alkoholen, aromatischen Kohlenwasserstoffen, Alkanen, Ketonen, Estern, Glykolethern und cyclischen Dimethylpolysiloxanen.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Säure ausgewählt ist aus Borsäure, Kohlensäure, Chlorwasserstoffsäure, Iodsäure, Salpetersäure, salpetriger Säure, Phosphorsäure, phosphoriger Säure, Schwefelsäure und schwefliger Säure.

6. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Säure ausgewählt ist aus Essig-, Benzoe-, Butter-, Zitronen-, Ameisen-, Milch-, Malein-, Naphthoe-, Oxal-, Phthal-, Pikrin-, Propion-, Bernstein-, Wein-, Toluyl-, Toluolsulfon- und Trifluoressigsäure.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei die Säure in einer Menge zwischen 0,01 und 0,1 Gewichtsteilen zugesetzt wird.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Harzlösung weiterhin Vorprodukte für modifizierende keramische Oxide enthält, die ihrerseits eine Verbindung mit einem Element enthalten, das aus Titan, Zirconium,

Aluminium, Tantal, Vanadium, Niobium, Bor und Phosphor ausgewählt ist, wobei die Verbindung mindestens einen hydrolysierbaren Substituenten enthält, der aus Alkoxy oder Acyloxy ausgewählt ist, und die Verbindung in einer solchen Menge vorhanden ist, daß die Beschichtung 0,1 bis 30 Gewichtsprozent modifizierendes keramisches Oxid enthält.

9. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Harzlösung weiterhin einen Platin-, Rhodium- oder Kupferkatalysator in einer Menge zwischen 5 und 1.000 ppm Platin, Rhodium oder Kupfer enthält, bezogen auf das Gewicht des Hydrogensilsesquioxanharzes.

Revendications

1. Procédé de stabilisation d'une solution de résine d'hydrogénosilsesquioxane comprenant 0,1 à 100 parties en poids de résine d'hydrogénosilsesquioxane dans 100 parties en poids de solvant, caractérisé en ce que l'on ajoute 0,002 à 4 parties en poids d'acide à ladite solution de résine.

2. Procédé selon la revendication 1, dans lequel au moins 75 % des espèces polymères de la résine ont un poids moléculaire moyen en poids supérieur à 1 200.

3. Procédé selon la revendication 2, dans lequel au moins 75 % des espèces polymères de la résine ont un poids moléculaire moyen en poids compris entre 1 200 et 50 000.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le solvant est choisi dans le groupe constitué des alcools, des hydrocarbures aromatiques, des alcanes, des cétones, des esters, des étherglycols et des diméthylpolysiloxanes cycliques.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'acide est choisi dans le groupe constitué des acides borique, carbonique, chlorhydrique, iodique, nitrique, nitreux, phosphorique, phosphoreux, sulfurique et sulfureux.

6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'acide est choisi dans le groupe constitué des acides acétique, benzoïque, butyrique, citrique, formique, lactique, maléique, naphtoïque, oxalique, phtalique, picrique, propionique, succinique, tartrique, toluique, toluènesulfonique et trifluoroacétique.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel on ajoute l'acide en une quantité comprise entre 0,01 et 0,1 partie en poids.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la solution de résine comprend, en outre, des précurseurs d'oxydes de céramique modificateurs comportant un composé contenant un élément choisi dans le groupe constitué du titane, du zirconium, de l'aluminium, du tantale, du vanadium, du niobium, du bore et du phosphore, dans lequel le composé contient au moins un substituant hydrolysable choisi dans le groupe constitué des groupes alcoxyles et acyloxyles, le composé étant présent en une quantité telle que le revêtement contienne 0,1 à 30 pour cent en poids d'oxydes de céramique modificateurs.

9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la solution de résine contient, en outre, un catalyseur au platine, au rhodium ou au cuivre en une quantité comprise entre 5 et 1 000 ppm de platine, de rhodium ou de cuivre sur la base du poids de résine d'hydrogénosilsesquioxane.

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(54) STABILIZED HYDROGEN SILSESQUIOXANE RESIN SOLUTION

(57)Abstract:
PURPOSE: To obtain the resin soln. useful for silica-containing ceramic coating and stable even during long-term storage by compounding a solvent, a hydrogen silsesquioxane resin and a specific substance in a predetermined wt. ratio.

CONSTITUTION: A hydrogen silsesquoxane resin soln. is constituted by compounding 100 pts.wt. of a solvent (e.g.; toluene) pref. selected from alcohol, aromatic hydrocarbon, alkane, ketone, ester, glycol ether and cyclic dimethylpolysiloxane, 0.1-100 pts.wt. of a hydrogen silsesquioxane resin wherein pref. 75% or more of one kind of a polymer has a wt. average mol.wt. of 1,200-50,000 and 0.002-4 pts.wt. of an acid pref. selected from boric acid, carbonic acid, hydrochloric acid, iodic acid, (nitrous) nitric acid, (phosphorous) phosphoric acid and (sulfurous) sulfuric acid.

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